

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 939 139 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
01.09.1999 Bulletin 1999/35

(51) Int. Cl.⁶: C22C 9/06, B23K 35/30

(21) Application number: 99301447.1

(22) Date of filing: 26.02.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 26.02.1998 JP 4583198
29.01.1999 JP 2327799

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(54) Abrasion resistant copper alloy for build-up cladding on engine cylinder head

(57) The copper alloy contains: 6 - 15 wt% Ni; 1 - 5 wt% Si; 1 - 5 wt% (total) Mo, W, Ta, Nb, and/or V. The alloy may also contain 0.5 - 1.5 wt% Fe, 1 - 5 wt% Cr, 0.5 - 0.9 wt% Al, and 0.1 - 1.0 wt% P, which are obligatory when Ni is above 9 wt%. The alloy may also contain 1 - 10 wt% Mn and 0.01 to 0.1 wt% rare earth metal. A valve seat (2) is formed by build-up cladding by irradiating a laser beam on a powder (4) of the copper alloy, provided in the rim of a port (3) formed in an engine cylinder head (1). Due to the composition of the copper alloy, the valve seat (2) has few microcracks and excellent abrasion resistance.

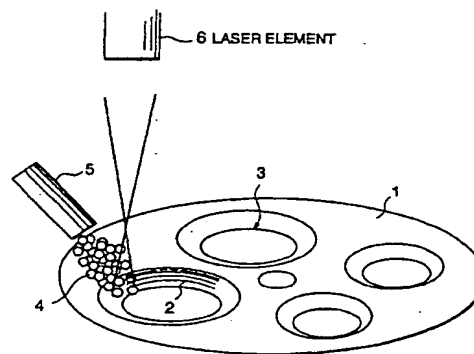


FIG.1

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Description

[0001] This invention relates to build-up cladding of a copper alloy for forming a valve seat in an engine cylinder head.

[0002] A method of forming a valve seat for an engine intake valve or exhaust valve is known wherein copper alloy powder is dissolved by a laser beam and accumulated on a cylinder head base metal along a rim of an intake port or exhaust port.

[0003] As an example of such a powdered copper alloy, Tokkai Hei 8-35027 published by the Japanese Patent Office in 1996 discloses a powder material comprising 10-30 wt% nickel (Ni), 0.5-5.0 wt% silicon (Si), and 2.0-15.0 wt% of at least one of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0004] This powder material may also comprise 2.0-15.0 wt% iron (Fe) or 1.0-10.0 wt% chromium (Cr). It may also comprise 0.01-0.1% misch metal or 0.1-1.0 wt% phosphorus (P), 1.0-10.0 wt% manganese (Mn), and 0.5-3.0 wt% boron (B). The remaining components are copper (Cu) and impurities.

[0005] According to tests performed by the inventors, a valve seat formed using this powder material displayed superior abrasion resistance, but microcracks occurred sporadically in the valve seat after cladding.

[0006] It would be desirable to be able to provide an abrasion resistant copper alloy in which microcracks rarely form.

[0007] It would also be desirable to be able, to improve the quality of an engine valve seat.

[0008] The present invention provides an abrasion resistant copper alloy consisting of copper (Cu), 6-9 wt% nickel (Ni), 1-5 wt% silicon (Si), and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0009] This invention also provides an abrasion resistant copper alloy consisting of copper (Cu), 6-9 wt% nickel (Ni), 1-5 wt% silicon (Si), 0.5-1.5 wt% iron (Fe), and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb) and vanadium (V).

[0010] This invention also provides an abrasion resistant copper alloy consisting of copper (Cu), 6-9 wt% nickel (Ni), 1-5 wt% silicon (Si), 0.5-1.5 wt% iron (Fe), 1-5 wt% chromium (Cr), and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0011] This invention also provides an abrasion resistant copper alloy consisting of copper (Cu), 6-9 wt% nickel (Ni), 1-5 wt% silicon (Si), 1-5 wt% chromium (Cr), 0.5-0.9 wt% aluminum (Al), and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0012] This invention also provides an abrasion resistant copper alloy consisting of copper (Cu), 6-9 wt% nickel (Ni), 1-5 wt% silicon (Si), 0.5-1.5 wt% iron (Fe), 0.5-0.9 wt% aluminum (Al), 5-15 wt% cobalt (Co), and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0013] This invention also provides an abrasion resistant copper alloy consisting of copper (Cu), 6-9 wt% nickel (Ni), 1-5 wt% silicon (Si), 0.5-1.5 wt% iron (Fe), 0.1-1.0 wt% phosphorus (P), and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0014] This invention also provides an abrasion resistant copper alloy consisting of copper (Cu), 6-9 wt% nickel (Ni), 1-5 wt% silicon (Si), 0.5-1.5 wt% iron (Fe), 1-5 wt% chromium (Cr), 0.1-1.0 wt% phosphorus (P), 1-10 wt% manganese (Mn), and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0015] This invention also provides an abrasion resistant copper alloy consisting of copper (Cu), 6-9 wt% nickel (Ni), 1-5 wt% silicon (Si), 0.5-1.5 wt% iron (Fe), 1-5 wt% chromium (Cr), 0.5-0.9 wt% aluminum (Al), 0.1-1.0 wt% phosphorus (P), 1-10 wt% manganese (Mn), 0.01-0.1 wt% rare earth metal, and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0016] This invention also provides an abrasion resistant copper alloy consisting of copper (Cu), 9-15 wt% nickel (Ni), 1-5 wt% silicon (Si), 0.5-1.5 wt% iron (Fe), 1-5 wt% chromium (Cr), 0.5-0.9 wt% aluminum (Al), 0.1-1.0 wt% phosphorus (P), and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0017] This invention also provides an abrasion resistant copper alloy consisting of copper (Cu), 9-15 wt% nickel (Ni), 1-5 wt% silicon (Si), 0.5-1.5 wt% iron (Fe), 1-5 wt% chromium (Cr), 0.5-0.9 wt% aluminum (Al), 0.1-1.0 wt% phosphorus (P), 1-10 wt% manganese (Mn), and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0018] This invention also provides an abrasion resistant copper alloy consisting of copper (Cu), 9-15 wt% nickel (Ni), 1-5 wt% silicon (Si), 0.5-1.5 wt% iron (Fe), 1-5 wt% chromium (Cr), 0.5-0.9 wt% aluminum (Al), 0.1-1.0 wt% phosphorus (P), 1-10 wt% manganese (Mn), 0.01-0.1 wt% rare earth metal, and 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V).

[0019] The above copper alloys are preferably provided in the form of powder for build-up cladding using a

laser beam.

[0020] Such build-up cladding is preferably used for forming a valve seat of intake and exhaust valves arranged in an engine cylinder head.

[0021] The details as well as other features and advantages of this invention are set forth in the remainder of the specification and are shown in the accompanying drawings.

Fig. 1 is a perspective view of a valve seat portion of an engine cylinder head.

Fig. 2 is a table showing the composition of copper alloy powder materials according to this invention.

Fig. 3 is a table showing the composition of comparative samples set by the inventors for the purpose of comparison.

Fig. 4 is a table showing the characteristics of the valve seats made of the powder materials of Fig. 2.

Fig. 5 is a table showing the characteristics of the valve seats made of the powder materials of Fig. 3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0022] Referring to Fig. 1 of the drawings, valve seats 2 for intake valves and exhaust valves are formed in an engine cylinder head 1. The valve seat 2 is formed by build-up cladding of copper alloy powder 4 having the composition of Samples #1 - #15 in Fig. 2 in the rim of a port 3 in the base material of the precast cylinder head 1.

[0023] Copper alloy powder 4 is supplied to the rim of the port 3 from a powder feed nozzle 5.

[0024] The building of copper alloy is formed with a thickness of 3mm or more on the rim of the hole 3 by irradiating this powder by a laser beam from a carbon dioxide laser element 6 under the following conditions.

Laser output = 5.0 kW

Working speed = 1.0 m/min

Shielding gas = Ar

Shielding gas flow rate = 20 liter/min

[0025] The base metal of the cylinder head 1 is cast in Al-Cu-Mg type alloy specified by AC2A, which is an aluminum casting alloy specified by JIS-H-5202. This cylinder head 1 is for an in-line type four-cylinder double overhead cam (DOHC) engine, and comprises four holes 3 for intake valves and exhaust valves in each cylinder.

[0026] The copper alloy powder 4 is formed as follows. First, molten copper alloy corresponding to one of Samples #1 - #15, which is a copper alloy according to this invention, shown in the table of Fig. 2, is prepared in a graphite pot of a high frequency induction furnace. Next, the molten copper alloy is allowed to flow down from the bottom of the pot, and "gas atomization" is performed wherein a gas is blown into the molten copper alloy

which is flowing down to pulverize the alloy to a powder. Dehydration, degassing, and particle grading is then performed to obtain a cladding powder.

[0027] A common feature of the copper alloy powders shown in Samples #1 - #15 of Fig. 2 is that they comprise 6-15 wt% nickel (Ni), 1-5 wt% silicon (Si), and 1-5 wt % of at least one of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb) and vanadium (V).

[0028] Nickel (Ni) is a useful element for improving the abrasion resistance of the valve seat 2.

[0029] By suppressing nickel (Ni) to 9 wt% or less, microcracks formed sporadically in the cladding layer can be reduced.

[0030] When the content of nickel (Ni) is higher than 9 wt%, the number of microcracks increases, but by further adding phosphorus (P) or manganese (Mn), 9-15 wt% of nickel (Ni) may improve the abrasion resistance of the alloy while suppressing the number of microcracks to within an acceptable range as shown by Samples #13 - #15. Nickel (Ni) or silicon (Si) cause deposition of hard silicides, but when nickel (Ni) is less than 6 wt%, deposition of hard silicides is reduced and high abrasion resistance is no longer obtained.

[0031] Silicon (Si) is required for deposition of hard silicides and is useful for improving the abrasion resistance of the valve seat 2. When the silicon (Si) content is less than 1 wt%, the deposition amount of hard silicides decreases, but if the content exceeds 5 wt%, abrasion resistance does not greatly improve and microcracks actually tend to form more easily.

[0032] By adding 0.5-1.5 wt% of iron (Fe) or 1-5 wt% chromium (Cr), abrasion resistance can be improved as shown by Samples #4 - #15 of Fig. 2. Both of these raise room temperature hardness and high temperature hardness of the cladding of a valve seat. When the addition amount is less than the lower limits mentioned above, a marked effect cannot be obtained from either iron (Fe) or chromium (Cr). However, when the upper limits are exceeded, there is not much improvement of hardness while microcracks form easily.

[0033] When 0.5-0.9 wt% of aluminum (Al) is added, room temperature hardness is enhanced and an improvement of abrasion resistance is obtained as shown by Samples #6, #7, and #12 - #15.

[0034] However, when aluminum (Al) is less than 0.5 wt%, the effect is small. When 0.9 wt % is exceeded, room temperature hardness decreases and microcracks form easily.

[0035] When 5-15 wt% of cobalt (Co) is added, lumps of hard silicides are deposited and room temperature hardness is mainly enhanced as shown by Samples #7 and #10 - #12. This is effective for abrasion resistance improvement of a valve seat of the exhaust valve. However, when the cobalt (Co) content is less than 5 wt% the effect is small, and when it exceeds 15 wt%, microcracks form easily.

[0036] When 0.1-1.0 wt% of phosphorus (P) is added, the viscosity decreases when the powder melts as

shown by Samples #8 - #15, so lumps of hard silicides are uniformly deposited when the cladding is formed by irradiation with the laser beam, and the formation of microcracks is suppressed. However, when the phosphorus (P) content is less than 0.1 wt% the effect is small, and when it exceeds 1.0 wt%, no further advantage is obtained.

[0037] When 1.0-10.0 wt% manganese (Mn) is added, the formation of microcracks is suppressed as shown by Samples #9 - #12, #14, and #15. However, when the manganese (Mn) content is less than 1 wt% the effect is small, and when it exceeds 10 wt%, no further advantage is obtained.

[0038] When 0.01-0.1 wt% of rare earth metals (REM) comprising misch metal is added, the formation of microcracks is suppressed as shown by Samples #10 - #12 and #15. However, when the rare earth metal (REM) content is less than 0.01 wt% the effect is small, and when it exceeds 0.1 wt%, no further advantage is obtained.

[0039] The remaining components of Samples #1 - #15 of Fig. 2 are copper (Cu) and impurities.

[0040] The inventors prepared 100 of the cylinder heads 1 for each Sample, and performed build-up cladding in sixteen ports 3 in each of the cylinder heads 1.

[0041] Build-up cladding was performed also using Comparative Samples #1 - #12 which are not according to this invention and which have the compositions shown in Fig. 3.

[0042] Comparative Sample #11 corresponds to the copper alloy disclosed in the aforesaid prior art Tokkai Hei 8-35027.

[0043] Comparative Samples #1 - #10 and #12 were arranged by the inventors for purposes of comparison, and do not necessarily conform to the prior art.

[0044] The remainder of the compositions of Comparative Samples #1 - #12 of Figs. 3 also comprises copper (Cu) and impurities.

[0045] The cylinder head 1 obtained by the above process was finished to predetermined dimensions and surface roughness via mechanical machining.

[0046] Twenty of the cylinder heads 1 which respectively have sixteen valve seats thus formed using the same powder were selected corresponding to each of the above Samples and Comparative Samples, and the number of microcracks was examined by performing a color check on the cladding layer of 320 of the holes 3 in total for each case.

[0047] The results are shown in Figs. 4 and 5.

[0048] The Vickers' hardness of the cladding, which has a significant correlation with the abrasion resistance of the valve seat formed, was measured at room temperature and at a high temperature of 400°C.

[0049] As for Samples #1 - #3 and Comparative Samples #1 - #4 which have a Vickers' hardness less than Hv150, the cladding was performed only in the valve seat of the intake valve.

[0050] The measurement results are shown in Figs. 4

and 5.

[0051] For each Sample and Comparative Sample, cylinder heads for which microcracks had not been found were subjected to the following engine test.

Engine = 1998cc in-line type four cylinder DOHC engine

Fuel = regular clear gasoline

Engine rotation speed = 6,000rpm

Intake valve material = heat-resistant steel corresponding to JIS SUH11

Exhaust valve material = heat-resistant steel corresponding to JIS SUH36

Engine load (throttle opening) = 4/4

Test time = 100 hours

[0052] After the test, the abrasion depth of the valve seat and valve face were measured.

[0053] The measurement results are shown in Figs. 4 and 5.

[0054] From the test results, the number of valve seats with microcracks decreased for Samples #1 - #15 according to this invention compared to Comparative Samples #1 - #12.

[0055] The depth of abrasion of the valve seat and valve face after the engine test was also less for Samples #1 - #15 according to this invention than for Comparative Samples #1 - #12.

[0056] For a valve seat formed using Samples #1 - #15, the external appearance of the frictional sliding parts was almost smooth, and no abrasion defects or pits which would cause loss of seal tightness of the valve seat were observed.

[0057] On the other hand for Comparative Sample #1 wherein the nickel (Ni) content was less than 6 wt%, the hardness Hv200 at room temperature was extremely low, and the abrasion depth of the valve seat was very high as the abrasion resistance was incomplete.

[0058] The abrasion depth of the valve face was also large due to repeated sticking and peeling of the abrasive powder on the valve face.

[0059] In a valve seat according to Comparative Sample #2 wherein the nickel (Ni) content was 10 wt% or more and neither phosphorus (P) nor manganese (Mn) were present, there were a large number of microcracks and the abrasion depths of the valve seat and valve face due to the test were high. Further, in a valve seat according to Comparative Sample #12 wherein phosphorus (P) and manganese (Mn) are added, but the nickel (Ni) content exceeds 15 wt%, high abrasion resistance was obtained, but a considerable number of the valve seats had microcracks.

[0060] For a valve seat according to Comparative Sample #3 wherein the molybdenum (Mo) and tungsten (W) content was less than 1 wt%, there was little deposition of hard silicides and adequate abrasion resistance was not obtained. This valve seat therefore had a large abrasion depth, and a ring-shaped groove was

formed in the valve seat. The abrasion depth of the corresponding valve face was also large.

[0061] For a valve seat according to Comparative Sample #4 wherein the total amount of molybdenum (Mo), tungsten (W) tantalum (Ta), niobium (Nb), and vanadium (V) exceeded 5%, there were a large number of microcracks as in the case of the valve seat according to Comparative Sample 2. Although engine tests were performed using cylinder heads wherein microcracks had not been detected, the abrasion depth of the valve seat and valve face due to the test was high.

[0062] For a valve seat according to Comparative Sample 5 wherein the iron (Fe) content exceeded 1.5% and the chromium (Cr) content exceeded 5%, the abrasion depth of the valve seat was large as in the case of valve seats according to Comparative Samples #2 and #4.

[0063] It appears that a high iron (Fe) or chromium (Cr) content is not effective in improving hardness and abrasion resistance.

[0064] For a valve seat according to Comparative Sample #6 wherein the aluminum (Al) content exceeded 0.9%, the same result was obtained as for valve seats according to Comparative Samples #2 and #4.

[0065] The number of microcracks was highest for this Comparative Sample #6. For the valve seat according to Comparative Sample #6, the high temperature hardness fell considerably compared to the room temperature hardness, as shown in Fig. 5. Therefore, the abrasion depth of the valve seat and valve face of the exhaust valve which reaches a high temperature, was fairly large.

[0066] For a valve seat according to Comparative Sample #7 wherein the cobalt (Co) content exceeded 15%, the same characteristics were obtained as for a valve seat according to Comparative Samples #2, #4, #5, and #6.

[0067] Comparative Sample #8 was a copper alloy powder wherein the nickel (Ni), silicon (Si), molybdenum (Mo), iron (Fe), and chromium (Cr) content was that of the copper alloy according to this invention, to which less than 0.1% phosphorus (P), less than 1% manganese (Mn) and less than 0.01% rare earths (REM) had been added.

[0068] In a valve seat formed using this copper alloy powder, there was no particular decline of abrasion resistance, but there were numerous microcracks.

[0069] For a valve seat according to Comparative Sample #9 having an identical composition to that of Comparative Sample #8 wherein the phosphorus (P) content had been increased to more than 1.0 wt%, there were few microcracks but the abrasion resistance was not high enough.

[0070] For a valve seat according to Comparative Sample 10 having an identical composition to that of Comparative Sample 8 wherein the manganese (Mn) content had been increased to more than 1.0 wt%, there

was also no great improvement compared to Comparative Sample 8.

[0071] For a valve seat according to Comparative Sample 11 corresponding to the copper alloy disclosed in Tokkai Hei 8-35027 of the aforementioned prior art, there were a considerable number of microcracks.

[0072] Therefore, in a valve seat formed with the copper alloy of Samples #1 - #15 according to the present invention, excellent quality is obtained both in terms of the number of microcracks and the abrasion depth.

[0073] The contents of Tokugan Hei 10-45831 with a filing date of February 26, 1998 in Japan and Tokugan Hei 11-23277 with a filing date of January 29, 1999 in Japan are hereby incorporated by reference.

[0074] Although the invention has been described above by reference to certain embodiments of the invention, the invention is not limited to the embodiments described above. Modifications and variations of the embodiments described above will occur to those skilled in the art, in light of the above teachings.

Claims

1. An abrasion resistant copper alloy consisting of:

6-9 wt% nickel (Ni);
1-5 wt% silicon (Si);
1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V); and
copper (Cu).

2. An abrasion resistant copper alloy consisting of:

6-9 wt% nickel (Ni);
1-5 wt% silicon (Si);
1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V);
0.5-1.5 wt% iron (Fe); and
copper (Cu).

3. An abrasion resistant copper alloy consisting of:

6-9 wt% nickel (Ni);
1-5 wt% silicon (Si);
1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V);
0.5-1.5 wt% iron (Fe);
1-5 wt% chromium (Cr); and
copper (Cu).

4. An abrasion resistant copper alloy consisting of:

6-9 wt% nickel (Ni);
1-5 wt% silicon (Si);

- 1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V);
1-5 wt% chromium (Cr);
0.5-0.9 wt% aluminum (Al); and
copper (Cu).
5. An abrasion resistant copper alloy consisting of:
- 6-9 wt% nickel (Ni);
1-5 wt% silicon (Si);
1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V);
0.5-1.5 wt% iron (Fe);
0.5-0.9 wt% aluminum (Al);
5-15 wt% cobalt (Co); and
copper (Cu).
6. An abrasion resistant copper alloy consisting of:
- 6-9 wt% nickel (Ni);
1-5 wt% silicon (Si);
1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V);
0.5-1.5 wt% iron (Fe);
0.1-1.0 wt% phosphorus (P); and
copper (Cu).
7. An abrasion resistant copper alloy consisting of:
- 6-9 wt% nickel (Ni);
1-5 wt% silicon (Si);
1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb) and vanadium (V);
0.5-1.5 wt% iron (Fe);
1-5 wt% chromium (Cr);
0.1-1.0 wt% phosphorus (P);
1-10 wt% manganese (Mn); and
copper (Cu).
8. An abrasion resistant copper alloy consisting of:
- 6-9 wt% nickel (Ni);
1-5 wt% silicon (Si);
1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V);
0.5-1.5 wt% iron (Fe);
1-5 wt% chromium (Cr);
0.5-0.9 wt% aluminum (Al);
5-15 wt% cobalt (Co);
0.1-1.0 wt% phosphorus (P);
1-10 wt% manganese (Mn);
0.01-0.1 wt% rare earth metal; and
copper (Cu).
9. An abrasion resistant copper alloy consisting of:
- 9-15 wt% nickel (Ni);
1-5 wt% silicon (Si);
1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V);
0.5-1.5 wt% iron (Fe);
1-5 wt% chromium (Cr);
0.5-0.9 wt% aluminum (Al);
0.1-1.0 wt% phosphorus (P); and
copper (Cu).
10. An abrasion resistant copper alloy consisting of:
- 9-15 wt% nickel (Ni);
1-5 wt% silicon (Si);
1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V);
0.5-1.5 wt% iron (Fe);
1-5 wt% chromium (Cr);
0.5-0.9 wt% aluminum (Al);
0.1-1.0 wt% phosphorus (P);
1-10 wt% manganese (Mn); and
copper (Cu).
11. An abrasion resistant copper alloy consisting of:
- 9-15 wt% nickel (Ni);
1-5 wt% silicon (Si);
1-5 wt% of a material selected from the group consisting of molybdenum (Mo), tungsten (W), tantalum (Ta), niobium (Nb), and vanadium (V);
0.5-1.5 wt% iron (Fe);
1-5 wt% chromium (Cr);
0.5-0.9 wt% aluminum (Al);
0.1-1.0 wt% phosphorus (P);
1-10 wt% manganese (Mn);
0.01-0.1 wt% rare earth metal; and
copper (Cu).

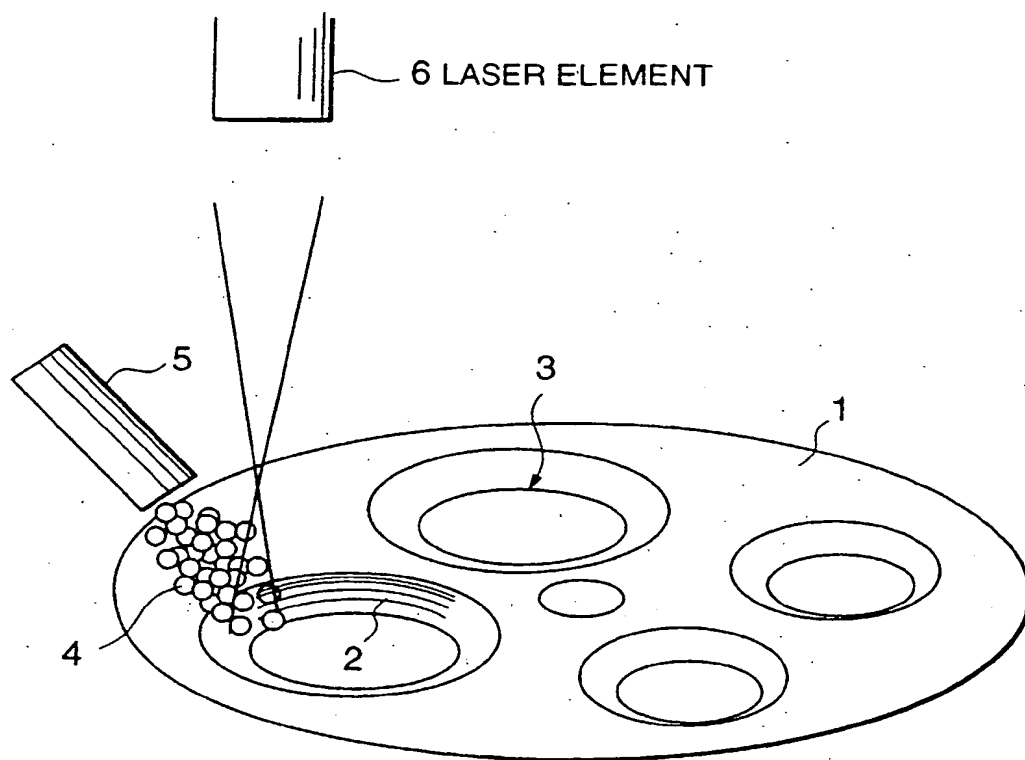


FIG.1

SAMPLES	CHEMICAL COMPONENT (WEIGHT %)													REM
	Ni	Si	Mo	W	Ta	Nb	V	Fe	Cr	Al	Co	P	Mn	
#1	6.1	4.8	4.5	-	-	-	-	-	-	-	-	-	-	-
#2	7.4	2.5	2.0	3.0	-	-	-	-	-	-	-	-	-	-
#3	8.2	3.3	-	2.5	2.4	-	-	-	-	-	-	-	-	-
#4	8.9	2.6	-	-	0.4	0.6	2.0	1.5	-	-	-	-	-	-
#5	9.0	2.4	-	-	0.8	1.5	0.5	1.3	2.5	-	-	-	-	-
#6	8.5	2.7	-	1.5	-	1.5	0.7	-	4.4	0.9	-	-	-	-
#7	9.0	2.6	-	-	-	1.9	2.2	1.5	-	0.5	10.2	-	-	-
#8	6.8	2.5	1.2	-	1.3	1.8	-	1.2	-	-	-	0.12	-	-
#9	7.7	2.4	1.4	1.2	-	1.3	1.1	0.5	4.8	-	-	0.22	1.2	-
#10	6.4	1.4	1.2	1.3	1.1	-	1.4	1.2	1.0	0.8	5.4	0.96	2.2	0.08
#11	6.3	2.6	2.1	1.2	1.0	-	0.7	1.4	4.6	0.6	14.5	0.97	5.4	0.08
#12	7.4	2.8	1.5	0.5	1.2	1.4	0.4	1.1	5.0	0.7	8.2	0.95	9.5	0.07
#13	12.1	2.8	-	-	-	0.5	1.5	1.2	1.9	0.9	-	0.5	-	-
#14	13.7	3.1	-	-	-	-	2.1	1.1	2.0	0.8	-	0.4	3.5	-
#15	15	3.0	-	-	-	-	2.5	1.0	1.8	0.8	-	0.8	2.5	0.08

REMARKS : LANTHANUM(La) IS USED AS RARE EARTH METAL (REM)

FIG.2

COMPARATIVE		CHEMICAL COMPONENT (WEIGHT %)													
SAMPLES	Ni	Si	Mo	W	Ta	Nb	V	Fe	Cr	Al	Co	P	Mn	REM	
#1	5.3	0.9	1.3	-	-	1.4	-	-	-	-	-	-	-	-	
#2	10.3	2.6	2.4	-	-	1.3	-	-	-	-	-	-	-	-	
#3	7.6	2.6	0.2	0.2	-	-	-	-	-	-	-	-	-	-	
#4	8.8	5.6	0.7	1.5	2.5	1.6	0.3	-	-	-	-	-	-	-	
#5	9.3	2.5	1.5	-	-	-	-	2.1	6.4	-	-	-	-	-	
#6	8.2	2.4	1.3	1.4	-	0.5	-	1.4	4.2	1.3	-	-	-	-	
#7	7.8	2.6	1.2	2.5	-	-	-	1.5	4.4	0.7	16.4	-	-	-	
#8	11.0	2.4	4.1	-	-	-	-	1.4	3.2	-	-	0.04	0.3	0.004	
#9	10.2	5.5	4.0	2.1	-	-	-	1.3	4.4	-	-	1.97	10.3	0.08	
#10	9.3	2.6	3.5	-	-	-	-	0.7	4.5	-	-	0.8	11.4	0.18	
#11	12.2	3.2	-	-	-	1.5	-	-	-	1.2	10.5	-	-	-	
#12	16.2	3.1	-	-	-	-	2.8	1.2	2.0	0.9	-	0.9	3.6	0.07	
REMARKS : LANTHANUM(La) IS USED AS RARE EARTH METAL (REM)															

REMARKS : LANTHANUM(La) IS USED AS RARE EARTH METAL (REM)

FIG.3

SAMPLES	NOS. OF VALVE SHEETS WITH CRACKS	VICKERS' HARDNESS		ABRASION DEPTH (μm)			
		ROOM TEMP.	400°C (HV)	INTAKE VALVE		EXHAUST VALVE	
				VALVE SHEET	VALVE FACE	VALVE SHEET	VALVE FACE
#1	2	225	122	39	18	-	-
#2	5	237	136	31	25	-	-
#3	8	244	128	28	28	-	-
#4	9	259	199	22	17	41	38
#5	7	265	211	25	22	38	33
#6	11	298	225	13	23	33	28
#7	10	287	254	17	18	18	15
#8	0	253	190	25	27	45	27
#9	0	259	203	21	26	39	36
#10	9	305	247	10	24	17	18
#11	6	288	258	16	16	14	14
#12	8	299	251	15	20	15	14
#13	15	285	239	12	18	12	14
#14	17	292	245	8	12	9	11
#15	18	298	251	8	10	8	13

FIG.4

NOS. OF COMPARATIVE VALVE SHEETS	VICKERS' HARDNESS		ABRASION DEPTH (μm)			
	(Hv)		INTAKE VALVE		EXHAUST VALVE	
	ROOM TEMP.	400°C	VALVE SHEET	VALVE FACE	VALVE SHEET	VALVE FACE
SAMPLES WITH CRACKS						
#1	2	188	103	96	68	-
#2	75	241	142	33	42	-
#3	5	191	130	79	57	-
#4	88	254	145	38	35	-
#5	84	268	218	24	20	30
#6	98	310	197	32	40	72
#7	72	286	266	35	37	58
#8	69	262	213	38	39	61
#9	16	273	229	39	48	55
#10	48	258	201	37	44	54
#11	94	277	208	45	43	56
#12	36	305	268	7	10	12

FIG.5

(19)



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(11)

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(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
12.01.2000 Bulletin 2000/02

(51) Int. Cl.⁷: C22C 9/06, B23K 35/30

(43) Date of publication A2:
01.09.1999 Bulletin 1999/35

(21) Application number: 99301447.1

(22) Date of filing: 26.02.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 26.02.1998 JP 4583198
29.01.1999 JP 2327799

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(54) **Abrasion resistant copper alloy for build-up cladding on engine cylinder head**

(57) The copper alloy contains: 6 - 15 wt% Ni; 1 - 5 wt% Si; 1 - 5 wt% (total) Mo, W, Ta, Nb, and/or V. The alloy may also contain 0.5 - 1.5 wt% Fe, 1 - 5 wt% Cr, 0.5 - 0.9 wt% Al, and 0.1 - 1.0 wt% P, which are obligatory when Ni is above 9 wt%. The alloy may also contain 1 - 10 wt% Mn and 0.01 to 0.1 wt% rare earth metal. A valve seat (2) is formed by build-up cladding by irradiating a laser beam on a powder (4) of the copper alloy, provided in the rim of a port (3) formed in an engine cylinder head (1). Due to the composition of the copper alloy, the valve seat (2) has few microcracks and excellent abrasion resistance.

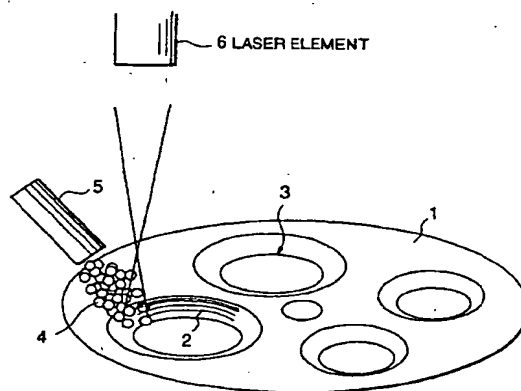


FIG. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 1447

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D, A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 06, 28 June 1996 (1996-06-28) -& JP 08 035027 A (NISSAN MOTOR CO LTD), 6 February 1996 (1996-02-06) * abstract *	1-11	C22C9/06 B23K35/30
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 02, 28 February 1997 (1997-02-28) -& JP 08 283889 A (CHUETSU GOKIN CHUKO KK), 29 October 1996 (1996-10-29) * abstract *	1,3,5	
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 06, 30 June 1997 (1997-06-30) -& JP 09 031571 A (HITACHI POWDERED METALS CO LTD; NISSAN MOTOR CO LTD), 4 February 1997 (1997-02-04) * abstract *	1,5	
A	EP 0 344 310 A (KOMATSU MFG CO LTD) 6 December 1989 (1989-12-06) * claims 1-3,7,13 *	1,4,6,7	C22C B23K
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 453 (C-0764), 28 September 1990 (1990-09-28) -& JP 02 179839 A (KOBELITE LTD), 12 July 1990 (1990-07-12) * abstract *	9-11	
A	EP 0 320 195 A (TOYOTA MOTOR CO LTD) 14 June 1989 (1989-06-14) * claims 1-4 * * examples 1-4 * * column 4, line 35 - column 9, line 12 * -/--	9-11	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 October 1999	Examiner Vlassi, E
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 1447

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 727 501 A (TOYOTA MOTOR CO LTD ; FUKUDA METAL FOIL POWDER (JP)) 21 August 1996 (1996-08-21) * claims 1-11 * * page 7, line 40 - page 13, line 45 *	9-11	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 October 1999	Examiner Vlassi, E
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/82 (P04C01)



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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



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LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 99 30 1447

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-8

Abrasion-resistant copper alloy with 6-9 wt% Ni, 1-5 wt% Si, 1-5 wt% Mo/W/Ta/Nb/V and optionally 0.5-1.5 wt% Fe, 1-5 wt% Cr, 0.5-0.9 wt% Al, 5-15 wt% Co, 0.1-1.0 wt% P, 1-10 wt% Mn, 0.01-0.1 wt% rare earth metal.

2. Claims: 9-11

Abrasion-resistant copper alloy with 9-15 wt% Ni, 1-5 wt% Si, 1-5 wt% Mo/W/Ta/Nb/V, 0.5-1.5 wt% Fe, 1-5 wt% Cr, 0.5-0.9 wt% Al, 0.1-1.0 wt% P and optionally 1-10 wt% Mn, 0.01-0.1 wt% rare earth metal.

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19-10-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 08035027 A	06-02-1996	NONE	
JP 08283889 A	29-10-1996	NONE	
JP 09031571 A	04-02-1997	NONE	
EP 0344310 A	06-12-1989	JP 63149347 A	22-06-1988
		DE 3789313 D	14-04-1994
		DE 3789313 T	21-07-1994
		WO 8804593 A	30-06-1988
JP 02179839 A	12-07-1990	JP 1778484 C	28-07-1993
		JP 4069219 B	05-11-1992
EP 0320195 A	14-06-1989	JP 1152232 A	14-06-1989
		JP 2639949 B	13-08-1997
		DE 3871099 A	17-06-1992
		US 5104748 A	14-04-1992
EP 0727501 A	21-08-1996	JP 8225868 A	03-09-1996
		AU 4559596 A	29-08-1996
		CA 2169513 A	18-08-1996
		CN 1143685 A	26-02-1997
		US 5843243 A	01-12-1998

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